

**TITLE**

**MOLECULAR CHEMICAL COMPOUNDS WITH STRUCTURES ALLOWING  
ELECTRON DISPLACEMENT AND CAPABLE OF EMITTING  
PHOTOLUMINESCENT RADIATION, AND PHOTOLUMINESCENCE  
QUENCHING DEVICE EMPLOYING THE SAME**

## **CLAIM OF PRIORITY**

7 [0001] This application makes reference to, incorporates the same herein, and claims all  
8 benefits accruing under 35 U.S.C. §119 from an application for *MOLECULAR CHEMICAL*  
9 *COMPOUNDS WITH STRUCTURES ALLOWING ELECTRON DISPLACEMENT AND*  
10 *CAPABLE OF EMITTING PHOTOLUMINESCENT RADIATION, AND*  
11 *PHOTOLUMINESCENCE QUENCHING DEVICE EMPLOYING THE SAME* earlier filed in  
12 the European Patent Office on 29 January 2003 and there duly assigned Serial No. 03 090  
13 022.9, and earlier filed in the Korean Intellectual Property Office on 27 August 2003 and  
14 there duly assigned Serial No. 2003-59486.

## BACKGROUND OF THE INVENTION

## 16 1. Field of the Invention

[0002] The invention relates to molecular chemical compounds for optical devices, which

1 have structures allowing electron displacement and capable of emitting photoluminescent  
2 radiation, and photoluminescence quenching devices (display devices) employing the same.

3 2. Description of the Related Art

4 [0003] Chemical compounds possessing the property of absorbing high-energy radiation (UV  
5 radiation, X-ray radiation, cathode radiation, etc.) and transforming the same into  
6 longer-wave, normally visible, radiation are referred to as luminophores. The process is  
7 called luminescence. Luminescence processes can be classified as to the type of energy  
8 supply. For example, in photoluminescence, an electron is promoted to a higher energy level  
9 by optical excitation (irradiation), whereas, in electroluminescence, an electron is promoted  
10 to a higher energy level by applying an electric field.

11 [0004] Photoluminescence quenching devices (PQDs) are known as a display device  
12 applying photoluminescence technology used under outdoor conditions, e.g., in strong  
13 sunlight. The photoluminescence quenching devices use exterior light to generate  
14 photoluminescent light which can be modulated by means of an applied voltage. These  
15 display devices can be operated in an auto-emissive mode which can be utilized under  
16 conditions where exterior light is sparse or absent.

1 [0005] The basic principle of the photoluminescence quenching device is well known. It  
2 involves a mechanism wherein splitting of the excited state permits controlling the intensity  
3 of emitted light. Such splitting produces charge carriers which are removed via the contacts.  
4 Hence, the mechanism of the photoluminescence quenching device proceeds inversely to that  
5 of an organic light-emitting diode (OLED) wherein charge carriers undergo recombination  
6 with emission of light.

7 [0006] Conjugated polymers selected from materials having a poly(phenylenevinylene)  
8 (PPV) or polyfluorene (PFO) basic structure are presently used as materials in PQDs.  
9 However, these materials have been developed for use in polymer organic light-emitting  
10 diodes (PLEDS) and show fluorescence quenching of more than 70% only at relatively high  
11 electric fields of  $2.5 \times 10^8$  V/m when used in PQD devices.

12 [0007] Donor-acceptor structures having non-linear optical properties were disclosed. Chiral  
13 materials for non-linear optical uses were disclosed by Stewart et al. in U.S. Pat. No.  
14 6,288,206B1 and polymers for non-linear optical uses were disclosed by Sasaki in U.S. Pat.  
15 No. 5,745,629A. However, emission of photoluminescent radiation is of secondary  
16 importance in these patents because the field dependence of the absorption and, in particular,

1 that of the refractive index are to be utilized with priority. The compounds which exhibit very  
2 strong donor-acceptor interactions even in the ground state of the material are not appropriate  
3 for photoluminescence quenching devices because these compounds are non-emissive due to  
4 high polarity.

5 **SUMMARY OF THE INVENTION**

6 [0008] It is therefore an object of the present invention to provide an improved material for a  
7 photoluminescence quenching device and an improved photoluminescence quenching device  
8 using the material.

9 [0009] It is another object of the present invention to provide chemical compounds enabling  
10 amplification of coupling between the electric field and the excited state.

11 [0010] It is a further object to provide for chemical compounds which allow for modulation  
12 of photoluminescent light by means of an electric field in a photoluminescence quenching  
13 device (PQD) and provide high photoluminescence quantum yields while ensuring high  
14 fluorescence quenching, lowering the electric field required for photoluminescence  
15 quenching, and exhibiting luminescent properties.

1 [0011] The present invention may be constructed with chemical compounds having a system  
2 including readily displaceable electrons which, in their excited states, furnish a desired dipole.  
3 The structure of the chemical compound includes an electron-rich donor group (electron  
4 donor group), an electron-deficient acceptor group (electron acceptor group), and a  
5 conjugated bridging element which bridges between the electron donor group and the  
6 electron acceptor group.

7 [0012] The chemical compounds of the present invention are designed in such a fashion that  
8 no significant dipole moment is produced by their donor/acceptor character in the ground  
9 state, but only develops in the excited state.

10 [0013] Preferably, the electron donor group is an aromatic amine or a fused cyclic system.  
11 More preferably, the electron donor group is triphenylamine, phenylenediamine, benzidine,  
12 carbazole, thiophene, and oligomers thereof.

13 [0014] The conjugated bridging element includes a  $\pi$ -conjugated carbon bond which is  
14 preferably included in an organic polymer with a chemical basic structure selected from the  
15 group consisting of a phenylenevinylene moiety in the form of a monomer, an oligomer, a  
16 polymer and a substituted product thereof, a phenylene moiety in the form of a monomer, an

1 oligomer, a polymer and a substituted product thereof, a fluorene moiety in the form of a  
2 monomer, an oligomer, a polymer and a substituted product thereof, a vinylene moiety in the  
3 form of a monomer, an oligomer, a polymer and a substituted product thereof, a ethinylene  
4 moiety in the form of a monomer, an oligomer, a polymer and a substituted product thereof,  
5 an anthranylene moiety in the form of a monomer, an oligomer, a polymer and a substituted  
6 product thereof, and a naphthylene moiety in the form of a monomer, an oligomer, a polymer  
7 and a substituted product thereof.

8 [0015] The electron acceptor group preferably includes monosubstituted phenyl,  
9 disubstituted phenyl, trisubstituted phenyl, imide and anhydride of aromatic polycarboxylic  
10 acid, oxazole, and a fused cyclic system. More preferably, the electron acceptor group has a  
11 chemical basic structure selected from the group consisting of fluorine-substituted phenyl,  
12 nitro-substituted phenyl, cyano-substituted phenyl, imide and anhydride of  
13 perylenetetracarboxylic acid and a substituted compound thereof, imide and anhydride of  
14 naphthalenetetracarboxylic acid and a substituted compound thereof, oxadiazole and a  
15 substituted compound thereof, oxazole and a substituted compound thereof, and a  
16 fluorenylidene moiety and a substituted compound thereof.

1 [0016] The above chemical compounds can be used for a photoluminescence quenching  
2 device. The preferred embodiment of the photoluminescence quenching device includes a  
3 glass substrate, a conductive transparent indium-tin oxide (ITO) layer on the glass substrate, a  
4 poly(ethylenedioxythiophene)/polystyrenesulfonic acid conductive polymer layer with a  
5 thickness of about 30 to about 100 nm on the conductive transparent indium-tin-oxide layer,  
6 an emitter layer comprising the chemical compounds having the donor-acceptor structure  
7 with a thickness of from 50 to 150 nm, and a metal contact. More than half of the emitted  
8 photoluminescent radiation may be suppressed when applying a voltage of 15 volts.

9 **BRIEF DESCRIPTION OF THE DRAWINGS**

10 [0017] The above aspect and advantages of the present invention will become more apparent  
11 by describing in detail preferred embodiments thereof with reference to the attached drawings  
12 in which:  
13 [0018] FIG. 1 is a diagram illustrating a functional principle of a photoluminescence  
14 quenching device according to the present invention; and  
15 [0019] FIG. 2 illustrates a basic configuration of a donor-acceptor structure according to the

1 present invention.

2 **DETAILED DESCRIPTION OF THE INVENTION**

3 [0020] Owing to the structure of a donor/conjugated bridging element/acceptor, the  
4 compound of the present invention is particularly suitable for use in a photoluminescence  
5 quenching device (PQD). Stronger coupling is achieved by higher bulkiness and a more  
6 dipolar character in the excited state. In the excited state, the applied exterior electric field  
7 can act on the dipole and give rise to charge separation.

8 [0021] The basic principle of the PQD is illustrated in FIG. 1. In analogy to an OLED  
9 display, the design of a PQD is likewise very simple, in principle. The (extremely thin)  
10 molecular chemical layer is embedded between two metal films. Excited states are  
11 generated in the material by absorption of ambient light and may undergo radiative decay  
12 with emission of light. An electric field is created by applying a voltage to the two contacts.  
13 The electric field effects separation of the excited states into charge carriers which are  
14 removed via the contacts.

15 [0022] To avoid corrosion and chemical degradation, the entire structure is set up in an inert

1 gas atmosphere and encapsulated so as to be airtight. The better the sealing, the longer the  
2 expected service life of the device.

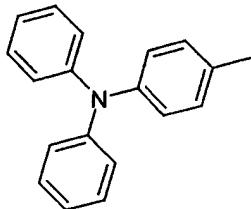
3 [0023] The structural set-up principle of the donor/conjugated bridging element/acceptor  
4 molecular chemical layer is illustrated in FIG. 2.

5 [0024] The preparation of the compounds according to the present invention is effected  
6 according to methods well-known to those skilled in the art. Thus, for example, the individual  
7 structural elements can be joined together using well-known modular systems. To this end,  
8 both oligomers or monomers and polymer structures can be created. Thin monomer and  
9 oligomer layers can be produced by vapor deposition in high vacuum. To this end,  
10 appropriate materials are evaporated in high vacuum from a heatable evaporation source and  
11 deposited as a compact thin film on substrates situated in a high vacuum. Typical basic  
12 pressures are in the range of from  $10^{-4}$  to  $10^{-9}$  mbars.

13 [0025] According to the invention, the chemical basic structures for such an electron donor  
14 group preferably are aromatic amines and fused cyclic systems. Preferably, the electron donor  
15 group includes (a) triphenylamine, (b) phenylenediamine or *p*-semidine  
16 (aminodiphenylamine) and (c) benzidine, (d) carbazole (dibenzopyrrole) and (e) thiophene

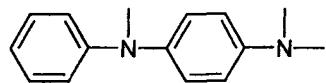
1 and its oligomers. The compounds having a basic structure of triphenylamine of formula 1a,  
2 phenylenediamine of formula 1b, benzidine of formula 1c, carbazole of formula 1d, and  
3 thiophene and its oligomers, represent classes of structures particularly suitable for the donor  
4 portion.

5 [Formula 1a]



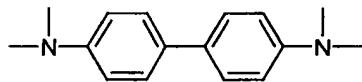
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7 [Formula 1b]



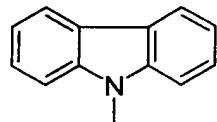
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9 [Formula 1c]



10

11 [Formula 1d]



12

13 [0026] The conjugated bridging elements according to the present invention are preferably

1 selected from the substance group of  $\pi$ -conjugated organic compounds.

2 [0027] More specifically, the compounds are selected from (a) phenylenevinylene moieties in

3 the form of monomers, oligomers, polymers and substituted products thereof, (b) phenylene

4 moieties in the form of monomers, oligomers, polymers and substituted products thereof, (c)

5 fluorene moieties in the form of monomers, oligomers, polymers and substituted products

6 thereof, (d) vinylene moieties in the form of monomers, oligomers, polymers and substituted

7 products thereof, (e) ethinylene moieties in the form of monomers, oligomers, polymers and

8 substituted products thereof, (f) anthranylene moieties in the form of monomers, oligomers,

9 polymers and substituted products thereof, and (g) naphthylene moieties in the form of

10 monomers, oligomers, polymers and substituted products thereof.

11 [0028] Especially suitable structural classes for a conjugated bridging element are the

12 compounds including (a) phenylenevinylene moieties of formula 2a in the form of monomers,

13 oligomers, polymers and substituted products thereof, (b) phenylene moieties of formula 2b

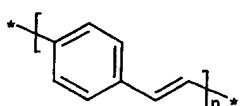
14 in the form of monomers, oligomers, polymers and substituted products thereof, (c) fluorene

15 moieties of formula 2c in the form of monomers, oligomers, polymers and substituted

16 products thereof, (d) vinylene moieties of formula 2d in the form of monomers, oligomers,

1 polymers and substituted products thereof, (e) ethinylene moieties of formula 2e in the form  
2 of monomers, oligomers, polymers and substituted products thereof, (f) anthranylene  
3 moieties of formula 2f in the form of monomers, oligomers, polymers and substituted  
4 products thereof, and (g) naphthylene moieties of formula 2g in the form of monomers,  
5 oligomers, polymers and substituted products thereof.

6 [Formula 2a]



7

8 wherein n is a number ranging from 1 to 20.

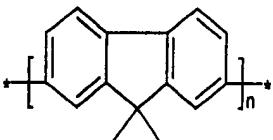
9 [Formula 2b]



10

11 wherein n is a number ranging from 1 to 20.

12 [Formula 2c]



13

14 wherein n is a number ranging from 1 to 20.

1 [Formula 2d]

2 \*

3 wherein n is a number ranging from 1 to 20.

4 [Formula 2e]

5 \*

6 wherein n is a number ranging from 1 to 20.

7 [Formula 2f]

8 \*

9 wherein n is a number ranging from 1 to 20.

10 [Formula 2g]

11 \*

12 wherein n is a number ranging from 1 to 20.

13 [0029] In the formulae above and below, an asterisk '\*' indicate the point of attachment of an

14 electron donor or an electron acceptor.

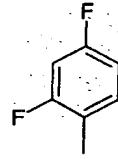
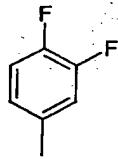
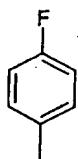
1 [0030] Preferred chemical basic structures for electron acceptor compounds are mono-, di-  
2 and/or trisubstituted phenyls, imides and anhydrides of aromatic polycarboxylic acids,  
3 oxazoles, as well as fused cyclic systems.

4 [0031] Preferably, they are (a) fluorine-substituted phenyl groups (mono-, di- and/or  
5 tri-substituted); (b) nitro-substituted phenyl groups, preferably *m*- and *p*-substituted phenyl  
6 groups; (c) cyano-substituted phenyl groups, preferably mono- or disubstituted phenyl  
7 groups; (d) imides and anhydrides of perylenetetracarboxylic acid, and substituted products  
8 thereof; (e) imides and anhydrides of naphthalenetetracarboxylic acid, and substituted  
9 products thereof; (f) oxadiazoles, and substituted products thereof; (g) oxazoles, and  
10 substituted products thereof; and (h) fluorenylidene moieties, and substituted products  
11 thereof.

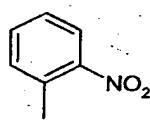
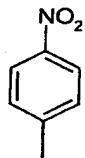
12 [0032] Especially suitable compounds of the electron acceptor groups include  
13 fluorine-substituted phenyl groups of formulae 3a-3c, nitro-substituted phenyl groups of  
14 formulae 3d and 3e, cyano-substituted phenyl groups of formulae 3f-3h, imides and  
15 anhydrides of perylenetetracarboxylic acid of formula 3i, imides and anhydrides of  
16 naphthalenetetracarboxylic acid of formula 3j, oxadiazoles of formula 3k and substituted

1 products thereof, oxazoles of formula 3l and substituted products thereof, and fluorenylidene  
2 moieties of formula 3m and substituted products thereof.

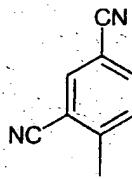
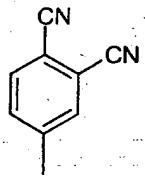
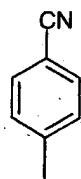
3 [Formula 3a] [Formula 3b] [Formula 3c]



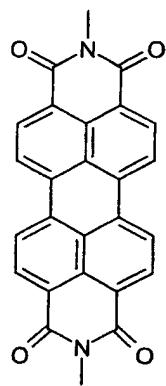
5 [Formula 3d] [Formula 3e]



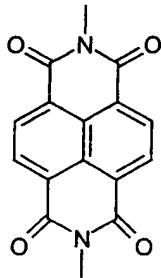
7 [Formula 3f] [Formula 3g] [Formula 3h]



9 [Formula 3i]

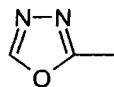


1 [Formula 3j]



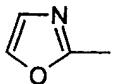
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3 [Formula 3k]



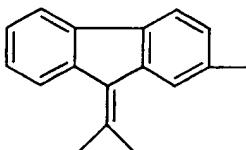
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5 [Formula 3l]



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7 [Formula 3m]



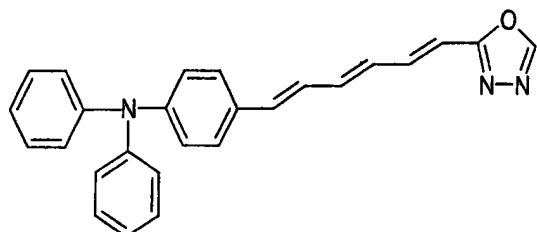
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9 [0033] More preferred chemical compounds with structures allowing electron displacement,  
10 capable of emitting photoluminescent radiation, are donor/bridge/acceptor structures in the  
11 form of oligomers and monomers of formulas 4a through 4c, as well as compounds including  
12 triphenylamine-oxadiazole combination of formula 5a having a donor and an acceptor in the

1 main chain of the polymer, phenylenediamine-trifluorobenzene combination of formula 5b  
2 having a donor and an acceptor in the main chain of the polymer, and  
3 benzidine-bis(oxadiazole) combination of formula 5c having a donor in the main chain and  
4 an acceptor in the side chain.

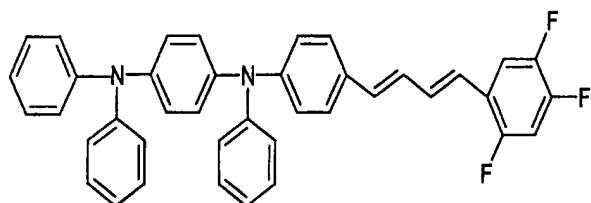
5 [0034] A non-symmetrical triphenylamine-oxadiazole combination of formula 4a, a  
6 non-symmetrical phenylenediamine-trifluorobenzene combination and a symmetrical  
7 phenylenediamine-bis(trifluorobenzene) combination have typical structures of  
8 donor-acceptor materials based on small molecules.

9 [Formula 4a]



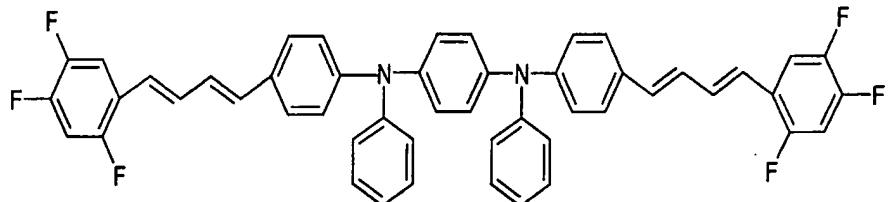
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11 [Formula 4b]



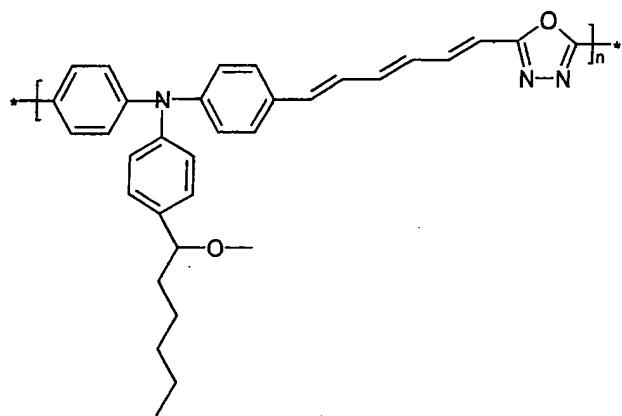
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1 [Formula 4c]



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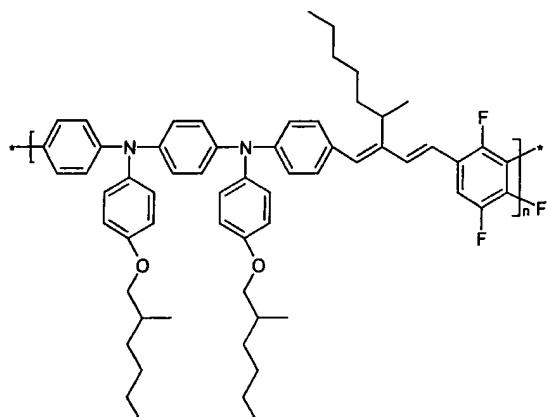
3 [Formula 5a]



4

5 wherein n is a number ranging from 100 to 2,000.

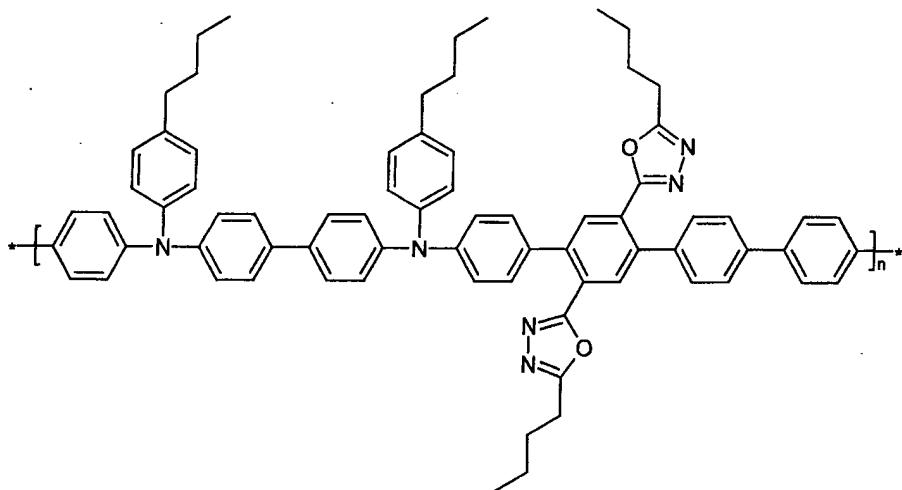
6 [Formula 5b]



7

1 wherein n is a number ranging from 100 to 2,000.

2 [Formula 5c]



3

4 wherein n is a number ranging from 100 to 2,000.

5 [0035] In another embodiment of the invention, the conjugated bridging element according to

6 the invention has an additional branched or side chain and a substitution incorporated therein

7 to improve the solubility. It is preferred to use branched alkyl and alkoxy groups preferably

8 with four to fourteen carbon atoms. The electron donor and acceptor groups may be linked to

9 the main chain of the bridging element, may be linked to the branched or side chain of the

10 bridging element or may be linked as a branched or side chain of the bridging element.

11 [0036] The compounds provided according to the invention are excellently suited for use in

12 photoluminescence quenching devices. They have luminescent properties, ensure high

1 fluorescence quenching, require the electric field of lower than  $1.5 \times 10^8$  V/m to quench half of  
2 the photoluminescent radiation emitted with no field, and, in addition, furnish high  
3 photoluminescence quantum yields. Typical fluorescence quantum yields are at values higher  
4 than 40%. Materials of the invention having the structures of formula 5a, 5b and 5c are found  
5 to be particularly suitable.

6 [0037] A photoluminescence quenching device (PQD) according to the invention, using a  
7 polymer emitter material integrated as a thin film in the PQD display device, has the  
8 following structure.

9 [0038] The display device is set up based on a transparent substrate, preferably a glass  
10 substrate coated with conductive transparent indium-tin oxide (ITO).

11 [0039] The ITO layer is spin-coated with a layer of  
12 poly(ethylenedioxythiophene)/polystyrenesulfonic acid conductive polymer. This layer  
13 serves to level any surface roughness. The preferred typical layer thickness ranges from 30 to  
14 100 nanometers.

15 [0040] The polymers of the invention are processed into thin films by spin-coating from a  
16 suitable organic solvent such as toluene, xylene, chloroform, or chlorobenzene. Subsequently,

1       a layer of emitter polymer in accordance with formula 5(a), 5(b) or 5(c) is spin-coated to a  
2       typical thickness of 50-150 nanometers.

3       [0041] The structure is completed by depositing a metal contact under high vacuum. The  
4       metals are selected from aluminum, calcium, ytterbium, silver, titanium, magnesium, zinc,  
5       and indium. It is also possible to use combinations of these metals and thin insulating layers  
6       made of fluorides and oxides of alkaline and alkaline earth metals.

7       [0042] Lithium fluoride with a thickness of one nanometer, deposited by thermal vapor  
8       deposition under high vacuum, is preferably used to this end. Onto this layer, preferably an  
9       aluminum layer with a typical thickness of 50-200 nanometers is coated by vapor deposition.

10      The structure is completed by an encapsulation, preferably glass, which is sealed with an  
11      adhesive so as to be gas-tight.

12      [0043] The structure emits photoluminescent radiation when irradiated with sunlight. The  
13      intensity of photoluminescence can be decreased by applying a voltage between the metal  
14      contact and ITO contact. The metal contact has positive polarity with respect to the ITO  
15      contact. When applying a voltage of 15 volts, more than half of the emitted photoluminescent  
16      radiation will be suppressed.

1 [0044] The compounds according to the invention are capable of readily displacing electrons,  
2 exhibit dipole character only in an excited state, and comprise chemical structures which  
3 represent electron donor/electron acceptor structures linked to each other via a conjugated  
4 bridging element. Since the compounds exhibit emissive properties, high photoluminescence  
5 quenching efficiency, and provide high photoluminescence quantum yields, the compounds  
6 are particularly suitable for use in photoluminescence quenching devices.

7 [0045] While the present invention has been particularly shown and described with reference  
8 to preferred embodiments thereof, it will be understood by those of ordinary skill in the art  
9 that various changes in form and details may be made therein without departing from the  
10 spirit and scope of the present invention as defined by the following claims.